



Oxidation of dichloromethane over Pt, Pd, Rh, and V₂O₅ catalysts supported on Al₂O₃, Al₂O₃–TiO₂ and Al₂O₃–CeO₂



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ABSTRACT

Pt, Pd, Rh and V₂O₅ metallic monolith catalysts supported on Al₂O₃, Al₂O₃–TiO₂ and Al₂O₃–CeO₂ were examined in the oxidation of dichloromethane (DCM). To improve the selectivity towards HCl and to prevent catalysts' deactivation, the water amount in the feed gas mixture was adjusted to 1.5 wt.%. All tested catalysts showed high activity in DCM oxidation and high selectivity towards HCl formation. Over Pt/Al₂O₃ and Rh/Al₂O₃, the 100% DCM conversions were reached at 420 °C and 440 °C and the maximum HCl yields detected were 92% and 93%, respectively. Addition of CeO₂ to the Al₂O₃ support affected the activity only a little, while somewhat more visible enhancement was seen with the addition of Pt, Pd, Rh and V₂O₅. However, more positive effect on the HCl and/or CO₂ yield was observed. Results showed that high acidity together with increased reducibility leads to an active catalyst for DCM oxidation. After the 40.3 h stability test no obvious change in the Pt/Al₂O₃ catalysts' performance was seen. Characterization showed no carbonaceous species on the catalyst's surface, but instead, some chlorine was detected on the surface that at this point did not affect the catalyst's activity or selectivity. The DCM decomposition seems to proceed on the catalyst surface via detaching the chlorine atoms before the breakage of the hydrogen bonds, hence following the order of the lowest bond energy in each step.

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1. Introduction

Chlorinated volatile organic compounds (CVOCs) are widely used in industry [1]. The three main chlorinated solvents used in Europe are methylene chloride (dichloromethane, DCM), perchloroethylene (PCE) and trichloroethylene (TCE) [2]. Of these three PCE (C₂Cl₄) was chosen as the model compound in our two previous studies [3,4] and now DCM (CH₂Cl₂) is studied over the same catalysts, since it is known to be present in industrial emissions as mixtures with PCE and other VOCs [5,6]. In the International Chemical Safety Cards (ICSC) [7] DCM is specified as an eye, skin and respiratory tract irritating chemical, which can cause lowering of consciousness and formation of methemoglobin. Long term or repeated exposure may cause dermatitis, has effects on the central nervous system and liver or may cause cancer to humans. Due to harmful properties the release of DCM is controlled by strict regulations, e.g. in EU [8], which are setting high demands for CVOC abatement systems.

Among the add-on technologies, low temperature catalytic oxidation can economically destroy the pollutants instead of only

removing them from gas for recycling them elsewhere in the biosphere [9–11]. In general, the catalysts applied in the CVOC destruction should be highly active, have high selectivity towards CO₂ and HCl formation and maintain high resistance towards deactivation. The role of the support is of special importance especially in DCM oxidation; for example over the Al₂O₃ catalyst DCM is known first to disproportionate on the surface (hydroxyl groups being the active sites) before the oxidation on the active phase [12–14]. To improve selectivity towards HCl, either a hydrogen-rich organic additive or water vapour should be added to the feed stream [5,10,15–19]. In addition to improved selectivity, water has been reported to stabilize, e.g. the Al₂O₃ supported catalyst by regenerating alumina hydroxyl groups consumed during the DCM decomposition [12–14].

In this study, the activity and selectivity of metallic monolith catalysts of Pt, Pd, Rh and V₂O₅ supported on three different washcoats, Al₂O₃, Al₂O₃–TiO₂ and Al₂O₃–CeO₂ were studied in dichloromethane (DCM, CH₂Cl₂) oxidation. Also the durability of the Pt/Al₂O₃ catalyst was investigated by performing a 40.3 h stability test. The main objective of this study was to study the catalytic properties having an influence on DCM oxidation in order to be able to develop even more efficient and environmentally friendly catalytic systems for the abatement of CVOCs. Before starting the tests, optimal operating conditions for the laboratory tests were

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studied with different H₂O and DCM concentrations and with several different space velocities (GHSV).

2. Experimental

2.1. Catalysts

In this study, the samples are the same as were previously tested with PCE oxidation in Refs. [3,4]. The metallic monolith catalysts with the cell density of 500 cpsi were prepared by Ecocat Ltd. The amount of support on the metal foil was set to be 24% of the total weight of the catalyst and three different washcoats used were Al₂O₃, Al₂O₃-TiO₂ (26 wt.% TiO₂) and Al₂O₃-CeO₂ (23 wt.% CeO₂). The noble metal loadings were fixed by the moles (*n*) and the targeted loadings were 1 wt.% with Pt-catalysts and 0.5 wt.% with Pd and Rh-catalysts. With vanadium-catalysts the targeted loading was 5 wt.%. More detailed information and the actual characteristics of the samples are presented in Refs. [3,4]. The summary of the characteristics of the samples is shown in Fig. 1.

2.2. Characterization

In the cases where the catalyst characterization was performed for the catalysts in their manufactured state, i.e. as metallic monoliths, only the washcoat was taken into account in the calculations. The catalysts were previously characterized by inductively coupled plasma-optical emission spectrometer (ICP-OES) by utilizing microwave-assisted aqua regia digestion [20], N₂ physisorption, CO or H₂ chemisorption, UV-vis diffuse reflectance spectroscopy (UV-vis DRS), temperature programmed isotopic oxygen exchange experiments, temperature programmed desorption of ammonia (NH₃-TPD) and temperature programmed reduction with H₂ (H₂-TPR). For more details about the procedures and the characterization results see Refs. [3,4].

In this study the Field Emission Scanning Electron Microscope (FESEM) equipped with Energy-Dispersive X-ray Spectroscopy (EDS) at an accelerating voltage of 15.0 kV was utilized to study the surface of Pt/Al₂O₃ monoliths before and after the 40.3 h stability test. Prior to analysis the samples were coated to avoid the accumulation of charge. In order to be able to detect the possible coke formation, additional set of samples was pretreated with Pt-sputtering in Argon atmosphere resulting in <10 nm Pt-layer on the samples.

The HSC Chemistry Software was used to calculate the decomposition enthalpy for one DCM molecule at room temperature in order to see the theoretical differences between bond energies of the atoms in the molecule. This method was used to estimate the formation of possible by-products during the oxidation reaction.

2.3. Activity experiments

Catalytic tests were performed in a tubular quartz reactor system operating under atmospheric pressure. Due to corrosive reaction products, all the materials used in the experimental set-up are corrosion resistant: quartz glass, heated Teflon piping (*T* = 180 °C) and Teflon connectors. In the vaporizer unit liquid VOC and water were fed with syringe pumps equipped with gas tight syringes to the heater for vaporization and to be mixed with air coming from a mass flow controller. The reaction temperature was measured outside the reactor, right before the monolith, and then corrected to represent the value inside the reactor. More detailed description of the experimental set up can be found in Ref. [3].

Dichloromethane (DCM, CH₂Cl₂, Algal, 99.0 area-%) was used as the model compound and all tests were performed in the presence of water to ensure the sufficient selectivity towards HCl. Before starting the activity tests, different testing conditions were

optimized for the laboratory scale studies. Water concentrations of 0.5 wt.%, 0.9 wt.%, 1.5 wt.%, 2.0 wt.%, 2.4 wt.% and 2.7 wt.% were tested with 500 ppm of DCM over the Pt/Al₂O₃ catalyst at 400 °C to optimize the water amount in the feed. The effect of DCM concentration (120 ppm, 500 ppm, 1055 ppm and 2145 ppm) was studied over the Pt/Al₂O₃ catalyst at 400 °C. Different gas hourly space velocities (GHSVs) of 16,000 h⁻¹, 24,000 h⁻¹, 32,000 h⁻¹, 40,000 h⁻¹ and 64,000 h⁻¹, calculated at room temperature (RTP) and normal pressure, were tested over the Pt/Al₂O₃ catalyst at 400 °C with 500 ppm of DCM. The change in GHSV between 16,000 h⁻¹ and 64,000 h⁻¹ was achieved by adjusting the feed flow from 0.54 l min⁻¹ to 2.14 l min⁻¹.

The experimental conditions during the activity tests were the following: the reaction mixture flow was set to 1.07 l min⁻¹ amounting to GHSV of 32,000 h⁻¹, the reaction temperature ranged from 100 °C to 700 °C (to 600 °C with the vanadium containing catalysts) and the heating rate used was 10 °C min⁻¹. The light-off tests were repeated at least once to verify the results and they were carried out over all the catalysts (12) and over all the supports (3). Before each test, the pre-treatment of the catalysts was done in air flow by heating up the catalyst from RTP to 700 °C (or to 600 °C with the V₂O₅ containing catalysts) and then cooling it down to RTP (or 100 °C) in air flow. During the 40.3 h stability test over the pre-treated Pt/Al₂O₃ catalyst, the oven temperature was set to 400 °C and the test was performed altogether during eight days in the following way: at the end of the day the gas flow (air + DCM + H₂O) was closed at the same time as the oven was switched off for the night, and next morning, after the oven temperature reached 400 °C, the gas flow was again introduced to the catalyst bed.

The gas analysis during the experiments was carried out with the Gasmet DX-4000 N FTIR analyser. The analyser was calibrated to detect the following chlorinated hydrocarbons: CH₂Cl₂, C₂Cl₄, C₂HCl₃, CHCl₃, CH₃Cl, COCl₂ and HCl. In addition, other VOCs and CO₂, CO, H₂O and NO_x are calibrated giving possibility to analyze all together 41 compounds. The detection limit of the calibrated compounds is 2 ppm, when the interference of unknown compounds is minimized. Due to the analysis the formation of Cl₂ was not measured and the complete closing of the chlorine-balance was not possible. The selectivity towards HCl, the desired end product, was followed by measuring the HCl concentration at the outlet and the HCl yield was calculated as follows:

$$Y_{\text{HCl}} = 100 \times \frac{c_{\text{HCl}}^{\text{out}}}{2 \times c_{\text{DCM}}^{\text{in}}} \quad (1)$$

where Y_{HCl} is the HCl yield [%], $c_{\text{HCl}}^{\text{out}}$ is the measured HCl concentration [ppm] and $c_{\text{DCM}}^{\text{in}}$ is the feed concentration of DCM [ppm].

3. Results and discussion

3.1. Properties of the catalysts

Metal loadings and dispersions, metallic surface areas and BET surface areas of the tested monoliths are shown in Fig. 1. More detailed results together with structural and textural properties and the results of UV-vis diffuse reflectance spectroscopy (DRS) and temperature programmed isotopic oxygen exchange experiments are presented in Ref. [3]. Details of the NH₃-TPD and H₂-TPR test results are given in Ref. [4]. The relationships of total acidity and reducibility to the catalysts activity in DCM oxidation is discussed in Section 3.4. Results from the FESEM-EDS characterization and nitrogen physisorption at -196 °C of the fresh and aged Pt/Al₂O₃ catalysts are presented in Section 3.6 together with the stability test results. The results of thermodynamic calculations are presented in Section 3.7 together with the DCM decomposition discussion.

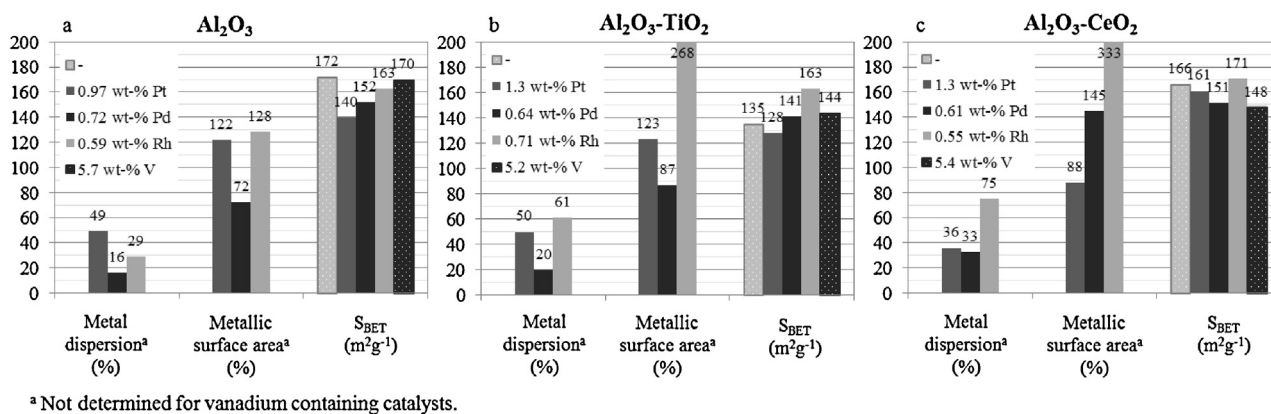


Fig. 1. Tested monoliths and their properties (the surface area (S_{BET}) of supports (–) were measured for powder samples). Catalysts and their properties have been discussed in detail in Ref. [3].

3.2. Effect of water feed concentration

Introduction of a hydrogen source into the reaction stream is of special importance when ensuring the formation of HCl and suppressing the unwanted side-product formation, but also when minimizing the deactivation of the catalyst [4,10,12–19]. The effect of different water concentrations on the DCM conversion, HCl yield and on the formation of methyl chloride (CH₃Cl), formaldehyde (CH₂O) and carbon monoxide (CO) can be seen in Fig. 2. (All yields were calculated in relation to the DCM feed.) As can be seen, the effect was mostly positive. The increase in the water concentration had no effect on the DCM conversion, but as expected, it increased the selectivity towards HCl. The formation of methyl chloride and CO was suppressed in the presence of increasing steam content. Based on the literature [18,19], the decrease in methyl chloride yield as a by-product was expected. The increase seen in the formaldehyde yield is probably due to increased hydrolysis caused by the increased amount of water in the reaction stream [12,21,22]. Another reason might be, that since both DCM and water (water molecule more efficiently) compete for the adsorption on the Lewis acid sites [12], where the formed formaldehyde intermediate is already chemisorbed, under these reaction conditions an increased amount of water enhances desorption of formaldehyde from the surface before its further reaction to CO or CO₂ [13]. No influence on the carbon dioxide (CO₂) formation was seen as its yield stayed stable at about 90%. Based on these results, the water feed in the laboratory experiments was set to 1.5 wt.%. Above 1.5 wt.% the HCl yield was enhanced only slightly if at all (see

Fig. 2) and the disadvantages such as unsteady H₂O evaporation and increased interference with the FTIR measurement appeared.

3.3. The effect of DCM concentration and GHSV

To examine the effect of reaction conditions on DCM oxidation at laboratory scale, experiments with different DCM concentrations and gas hourly space velocities (GHSV) over the Pt/Al₂O₃ catalyst at 400 °C in the presence of 1.5 wt.% of water were performed. The increasing of the DCM concentration influenced the catalyst activity and HCl selectivity only slightly, especially at concentrations from 100 ppm to 1000 ppm (Fig. 3). At the highest tested DCM concentration of 2145 ppm, the DCM conversion was seen to decrease from 94% to 90% and the HCl yield decreased from 82% to 75%. The CO₂ yield was seen to go down quite evenly from 98% to 62% as the DCM concentration was increased from 120 ppm to 2145 ppm (not shown in the figure). On methyl chloride and CO formation the effect of growing DCM concentration was more visible, and always negative, if the selectivity is considered. The increased methyl chloride amount with the growing DCM concentration was also reported by Wang et al. [19]. The slight decrease seen in the formaldehyde yield at 2000 ppm might be due to water content (1.5 wt.%) being insufficient to maintain efficient hydrolysis [12], especially, since now steam is increasingly needed to fulfil the growing demand for the hydrogen in the HCl formation [19].

The effect of increasing the GHSV was always negative on the activity and on the CH₃Cl, CH₂O and CO formation (Fig. 4). Also the

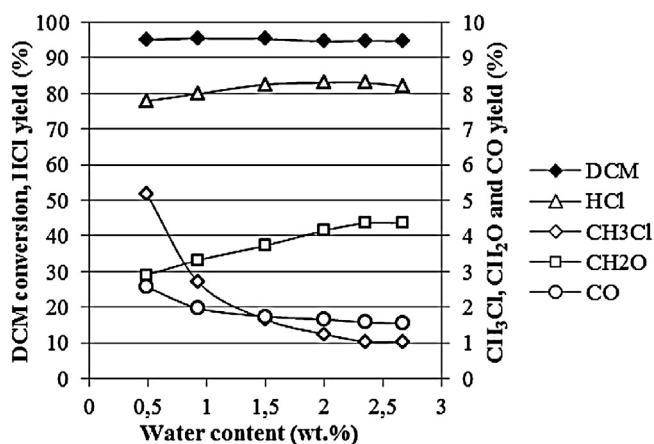


Fig. 2. The effect of water concentration on the DCM conversion and HCl, CH₃Cl, CH₂O and CO formation (Pt/Al₂O₃ catalyst, DCM 500 ppm, 400 °C, GHSV 32,000 h⁻¹).

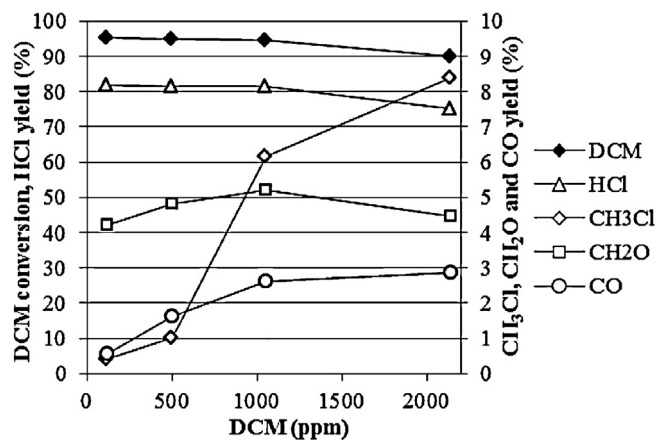


Fig. 3. The effect of DCM feed concentration on the DCM conversion and on the HCl, CH₃Cl and CO formation (Pt/Al₂O₃ catalyst, water feed 1.5 wt.%, 400 °C, GHSV 32,000 h⁻¹).

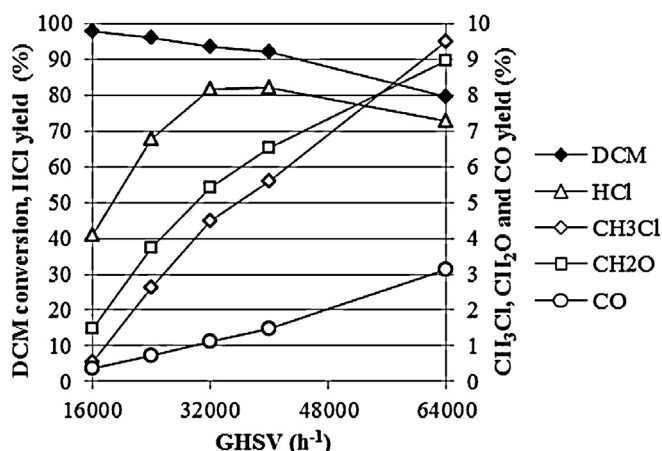


Fig. 4. The effect of different GHSVs on the DCM conversion and HCl, CH₃Cl, CH₂O and CO formation (Pt/Al₂O₃ catalyst, DCM 500 ppm, water feed 1.5 wt.%, 400 °C, GHSV 16,000, 32,000, 40,000 and 64,000 h⁻¹).

CO₂ yield was observed to decrease quite linearly from 100% to 50% as the GHSV was increased from 16,000 h⁻¹ to 64,000 h⁻¹. These results are in accordance with the results of other studies [23–25]. Instead, on the HCl yield, the effect was seen to be different: at the lower GHSV range, from 16,000 h⁻¹ up to 32,000 h⁻¹, raising the GHSV increased the HCl yield. The low HCl yields, 41% and 68%, observed at low GHSVs are probably due to the increased residence time in the catalyst bed giving more time for DCM to react to form aluminium chlorides instead of releasing Cl as HCl [12,13,26]. In this case, the reported values were recorded after 15 min and after 30 min of exposure at GHSVs of 16,000 h⁻¹ and 24,000 h⁻¹, respectively. During the stability test with GHSV of 32,000 h⁻¹ about 20 min was needed before the fresh γ -Al₂O₃ surface was saturated enough so that detected HCl and CH₃Cl concentrations were stable. For example, van den Brink et al. [13] reported that with 0.30 g of γ -Al₂O₃ in the gas flow of 50 ml min⁻¹ with the DCM concentration of 1000 ppm it took several hours before HCl appeared. To compare, in this study, the conditions were following: ~0.43 g Pt/ γ -Al₂O₃ catalyst (coated on the metallic monolith) at the gas flow of 1070 ml min⁻¹ with 500 ppm of DCM.

Based on these results, but also based on the knowledge from potential industrial applications [6], the reaction conditions for the activity experiments performed in the laboratory from now on were selected to be following: DCM concentration 500 ppm and GHSV 32,000 h⁻¹. Nevertheless, it must be remembered that these results and selected conditions are not directly applicable to the catalytic incinerator operating, e.g. with flow reversal [24,27].

3.4. Activity

The conversion curves during the DCM oxidation over all the tested catalysts are shown in Fig. 5a–c and the T_{50} and T_{90} temperatures are listed in Table 1. The results show that the supports (Al₂O₃, Al₂O₃-TiO₂ and Al₂O₃-CeO₂) themselves were very active in DCM

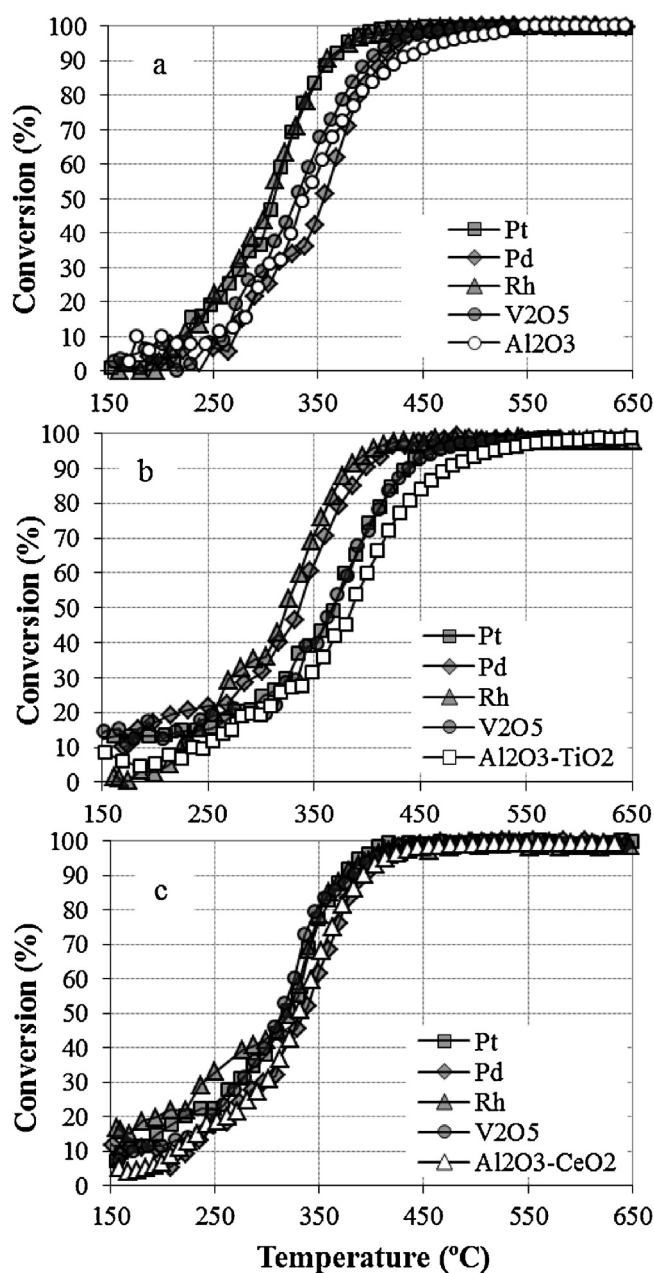


Fig. 5. The activity of all the (a) Al₂O₃, (b) Al₂O₃-TiO₂ and (c) Al₂O₃-CeO₂ supported catalysts (DCM 500 ppm, water 1.5 wt.%, GHSV 32,000 h⁻¹).

Table 1

T_{50} and T_{90} temperatures of tested catalysts (°C).

	Al ₂ O ₃		Al ₂ O ₃ -TiO ₂		Al ₂ O ₃ -CeO ₂	
	T_{50}	T_{90}	T_{50}	T_{90}	T_{50}	T_{90}
–	335	425	385	480	330	392
Pt	308	365	370	435	320	375
Pd	355	410	335	400	335	396
Rh	305	360	325	380	320	375
V ₂ O ₅	330	400	350	420	315	385

oxidation when compared e.g. to the thermal experiments reported in Ref. [5]. Now, e.g. at 450 °C the DCM conversion increased from only 10% up to 92%, 84% and 98% over Al₂O₃, Al₂O₃-TiO₂ and Al₂O₃-CeO₂, respectively. Hence, the activity order of different supports was Al₂O₃-CeO₂ > Al₂O₃ > Al₂O₃-TiO₂. High activity of the tested supports was expected since it has been previously reported by several authors [12–14,19,28]. For example with γ -Al₂O₃ van den Brink et al. [13] reported 100% DCM conversions already at 330 °C, Maupin et al. [14] saw complete DCM conversion at 380 °C and Wang et al. [19] reached 90% DCM conversions at 670 °C.

In Fig. 6a–b the relationship of the T_{50} temperature to total acidity and reducibility is presented. The activity order of the supports followed the measured values of acidity; the least active support was also the least acidic, especially when the weak acid sites are considered [4]. It is well known that surface acid sites are catalytically active centres for DCM decomposition [12–14,19,29–31].

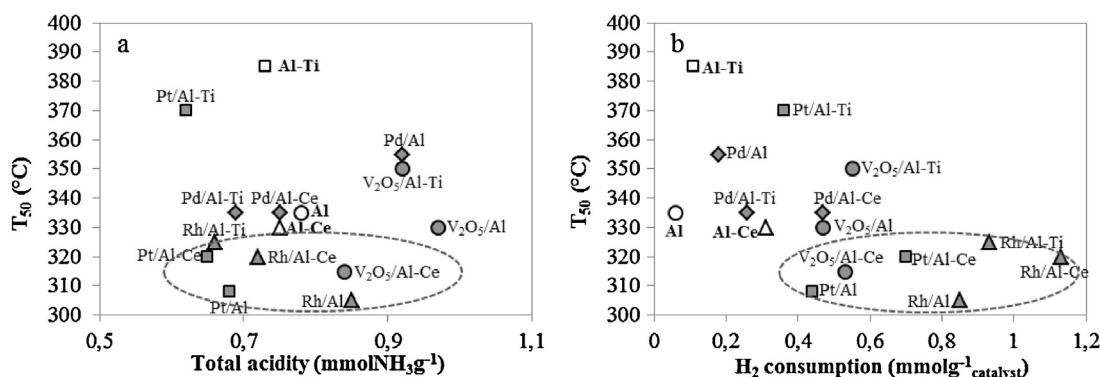


Fig. 6. Relationship between (a) total acidity and (b) H_2 consumption to T_{50} temperature (Al = Al_2O_3 , Al–Ti = Al_2O_3 – TiO_2 , Al–Ce = Al_2O_3 – CeO_2 , total acidity and H_2 consumption values are considered between 25 °C and 700 °C).

At this point the reducibility order of the supports did not correlate with the activity order, but the differences in H_2 consumption between the supports were small, especially below 500 °C where the DCM oxidation occurs. For example, the strongest enhancement in the reducibility seen with Al_2O_3 – CeO_2 raising the H_2 consumption value is at around 570 °C, which is due to the formation of non-stoichiometric CeO_x from CeO_2 (see Ref. [4]). The H_2 consumption in Fig. 6b is considered between 25 °C and 700 °C.

The addition of Pt, Pd, Rh and V_2O_5 affected the activity differently depending on the support (Fig. 5a–c, Table 1). On the Al_2O_3 support the effect was positive for all but the Pd catalyst and based on the T_{50} and T_{90} temperatures the activity order was in this case $Rh > Pt > V_2O_5 > Pd$. The temperatures needed to reach the 100% DCM conversions were 420 °C for Pt/ Al_2O_3 and 440 °C for Rh/ Al_2O_3 . When 26 wt.% of titania was introduced into the support, the activities of all but the Pd catalyst were decreased when compared to their corresponding Al_2O_3 supported catalysts (Fig. 5a–b, Table 1). The activity order of the catalysts supported over the Al_2O_3 – TiO_2 support was now $Rh > Pd > V_2O_5 > Pt$. Temperature of 460 °C was needed to reach 100% DCM conversion with the most active catalyst, Rh/ Al_2O_3 – TiO_2 .

The addition of 23 wt.% ceria into the support had only a small influence on the catalysts' activity (Fig. 5c, Table 1). When compared to the corresponding Al_2O_3 supported catalysts, the T_{50} temperatures of Pd and V_2O_5 were enhanced and the activity of Pt and Rh was decreased. Based on the T_{90} temperatures, the activity order of the catalysts supported on Al_2O_3 – CeO_2 was now $Rh = Pt > V_2O_5 > Pd$. To reach the 100% DCM conversions temperatures above 430 °C and 465 °C were needed over the Pt and Rh catalysts, respectively.

As it can be seen in Fig. 6a–b it is evident that the surface acidity plays an important role in the DCM oxidation, but high acidity alone is not enough to explain the catalysts' good activity (see e.g. Pd/ Al_2O_3). Also the increase in the reducibility correlates well with the catalysts' activity in DCM oxidation, but in such a way that acidity together with increased reducibility (see e.g. Pt/ Al_2O_3 and Rh/ Al_2O_3) leads to a highly active catalyst in DCM oxidation. This conclusion is supported by e.g. Chen et al. [28] as they studied series of CeO_2 – Al_2O_3 supported catalysts in DCM oxidation and reported that an optimal combination of surface acidity and redox property in the catalyst results in high activity in DCM oxidation. All vanadium containing catalysts showed rather high reducibility, but since the reduction peaks were centred at high temperatures, i.e. above 400 °C [4], the effect on the activity remained quite low. Vanadium catalysts being always the most acidic among their analogues, the small enhancement seen in activity with the vanadium catalysts (Fig. 5a–c) is probable due to the increased acidity. Metal dispersions were not observed to correlate with the activity orders

under these reaction conditions (Fig. 1). Also the lower Pt loading on Al_2O_3 (0.97 wt.% vs. 1.3 wt.%) had no influence on the activity. These results are in good agreement e.g. with Maupin et al. [14] as they observed no difference in DCM conversion when they tested the effect of different Pt loadings on γ - Al_2O_3 .

3.5. Selectivity

In total oxidation of chlorinated compounds the high activity is not enough, high demands are set to the selectivity of the catalyst as well. Analysis of the reaction products confirmed that over the tested catalysts the main oxidation products in DCM oxidation in moist conditions are CO_2 , CO and HCl. At the latest, at 99% DCM conversion, the only products detected were HCl and CO_2 , with an exception of V_2O_5 that still produced CO as an incomplete oxidation product. Depending on the catalysts also certain organic intermediate products, namely methyl chloride (CH_3Cl) and formaldehyde (CH_2O) were seen during the light-off tests at lower temperature regions, i.e. below 400–530 °C depending on the catalyst. The HCl yields during the DCM oxidation over all the catalysts are plotted in Fig. 7a–c. The by-product formation and the carbon balances for the experiments with Pt, Pd, Rh and V_2O_5 supported on Al_2O_3 are presented in Fig. 8a–d.

All the supports showed high selectivity towards CO, CO_2 and HCl. Over the Al_2O_3 – CeO_2 up to 100% CO_2 yield was reached at 590 °C followed by Al_2O_3 (detected maximum was 85% at 660 °C) and then Al_2O_3 – TiO_2 (maximum was 40% at 600 °C). Over the Al_2O_3 – CeO_2 support the HCl yield was 99% starting from 610 °C and over the Al_2O_3 – TiO_2 93% from 580 °C (see Fig. 7b–c). Over the Al_2O_3 the maximum HCl yield detected was 86% at 480 °C, but at a higher temperature range the HCl yield dropped and starting from 550 °C the yield was only from 74% to 78% (Fig. 7a).

The addition of Pt, Pd, Rh and V_2O_5 enhanced the HCl yields of all Al_2O_3 supported catalysts and now the selectivity to HCl was the highest among all noble metal or V_2O_5 loaded catalysts being above 90%, the maximum being 93% over Rh/ Al_2O_3 and 92% over Pt/ Al_2O_3 (Fig. 7a). Over both Al_2O_3 – TiO_2 and Al_2O_3 – CeO_2 supports, the addition of Pt, Pd, Rh or V_2O_5 was seen to enhance the HCl yields at the lower temperature range, but at temperatures above 480–530 °C and 380–430 °C, respectively, the effect was negative and the maximum HCl yields detected remained below 90% (Fig. 7b–c).

In this study the selectivity towards methyl chloride (CH_3Cl) over the supports followed the order of Al_2O_3 – CeO_2 < Al_2O_3 < Al_2O_3 – TiO_2 , as the methyl chloride yields over Al_2O_3 – CeO_2 were the lowest. The formation of methyl chloride was not seen over any Pd catalysts or with Pt/ Al_2O_3 – TiO_2 , Pt/ Al_2O_3 – CeO_2 or Rh/ Al_2O_3 – CeO_2 . Over all the V_2O_5 catalysts and over Al_2O_3 – CeO_2 support the methyl chloride concentrations

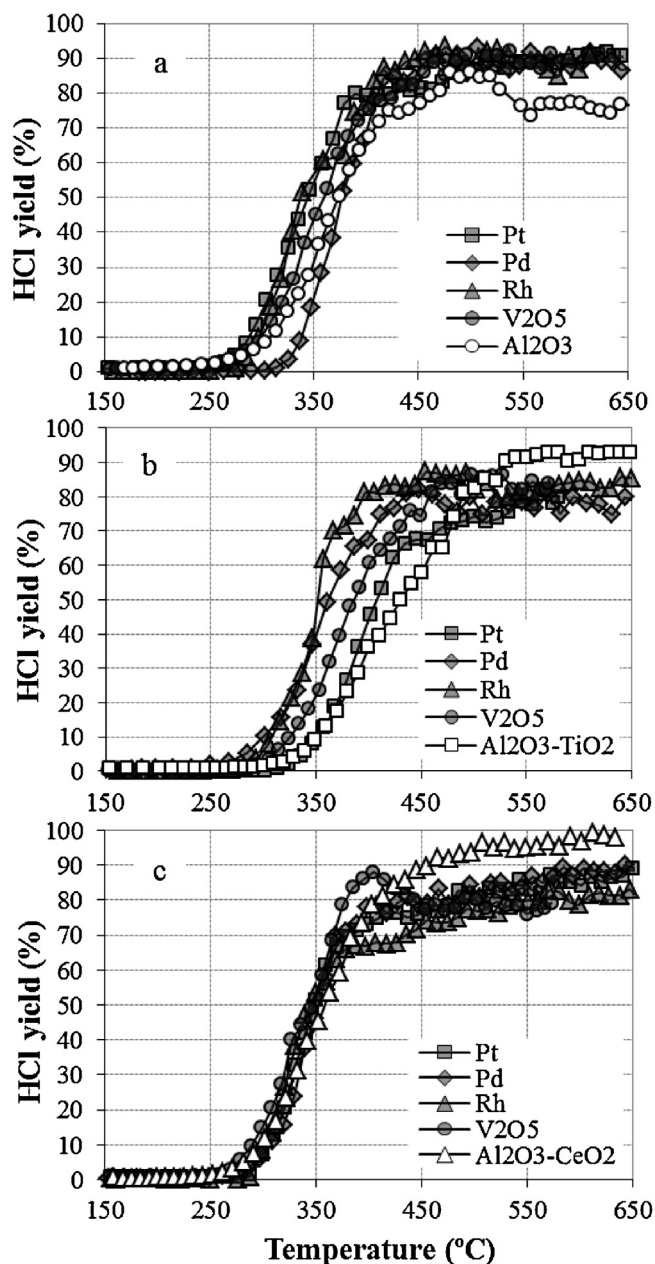


Fig. 7. The HCl yields of all the (a) Al_2O_3 , (b) $\text{Al}_2\text{O}_3\text{--TiO}_2$ and (c) $\text{Al}_2\text{O}_3\text{--CeO}_2$ supported catalysts (the same conditions as in Fig. 5).

were low; measured maximums being less than 10 ppm (yield being <2%) (see e.g. Fig. 8d). The highest detected methyl chloride yields were 13% at 340 °C over $\text{Pt}/\text{Al}_2\text{O}_3$ and 11% at 350 °C over $\text{Rh}/\text{Al}_2\text{O}_3$ (Fig. 8a and c). Methyl chloride was not detected any more at the temperatures above 450 °C over the Al_2O_3 supported catalysts and above 420 °C over $\text{Al}_2\text{O}_3\text{--TiO}_2$ and $\text{Al}_2\text{O}_3\text{--CeO}_2$ supported catalysts. Methyl chloride formation over Al_2O_3 supported catalysts under oxidative conditions has been described also before by several authors [13,14,18,19,30]. For example Maupin et al. [14] observed 32% yield of methyl chloride at 340 °C over 0.47Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst when feeding 1000 ppm of DCM in moist conditions (2.7 mol.% water) with the space velocity of 20,000 h^{-1} . Haber et al. [30] concluded in their study that the formation of methyl chloride is related to the amount of Lewis acid sites.

Formaldehyde (CH_2O) formation was seen over all the tested catalysts and the detected maximum concentrations varied from 4 ppm to 60 ppm (resulting to the yields from 0.8% to 12%),

depending on the catalyst. The highest formaldehyde yields were observed over $\text{Al}_2\text{O}_3\text{--TiO}_2$ (12% at 490 °C), $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3\text{--CeO}_2$ (12% at 375 °C) and over $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$ (11% at 370 °C). The lowest yields were always seen over the Pd catalysts (<2%). Also $\text{Pt}/\text{Al}_2\text{O}_3\text{--CeO}_2$ and $\text{Rh}/\text{Al}_2\text{O}_3\text{--CeO}_2$ showed low amounts of formaldehyde in the gas phase. With all noble metal or V_2O_5 loaded catalysts, formaldehyde formation was no longer detected above 530 °C, V_2O_5 catalysts being the most refractory. Over all Pd catalysts the formation of formaldehyde stopped already before the temperature reached 420 °C. Pinard et al. [21] reported formaldehyde formation in DCM oxidation over a bifunctional Pt/NaY catalyst as the DCM transformation occurred via a two-step process: DCM hydrolysis over NaY followed by the oxidation of formaldehyde into CO_2 and H_2O over metallic particles. In their later study [22] both formaldehyde and methyl chloride were seen as intermediates in DCM oxidation over the PtHFAU catalyst in moist air. They concluded that DCM is hydrolysed over Brønsted acid sites of zeolite into formaldehyde and HCl while the Lewis acid sites were responsible for the methyl chloride formation at the higher temperature region. Recently Maupin et al. [14] concluded that DCM oxidation over $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts occurs following the bifunctional mechanism: DCM disproportionation into CO, CH_3Cl and HCl following CH_3Cl and CO oxidation to CO_2 . According to van den Brink et al. [13] during the DCM oxidation over $\gamma\text{-Al}_2\text{O}_3$ chemisorbed formaldehyde is formed before it disproportionates to form surface methoxy and formate groups, which will then react further to CH_3Cl and CO or CO_2 . The existence of both weak and strong acid sites was detected for all of our catalysts [4]. Especially V_2O_5 catalysts showed the presence of the strong acid sites (acidity at the temperature range from 300 °C to 700 °C), more than others, which is in accordance with the selectivity towards the formaldehyde formation. Therefore it is possible that in our reaction conditions formaldehyde is formed through direct hydrolysis of DCM [22] or chemisorbed formaldehyde [13] is desorbed from the catalysts surface and detected as a by-product in the gas phase before its further oxidation into CO_2 .

The $\text{Al}_2\text{O}_3\text{--CeO}_2$ supported catalysts were the ones producing the lowest amounts of carbon monoxide (CO) and when different active phases were compared, Pd and Pt catalysts showed always the lowest selectivity towards CO formation. Over $\text{Pd}/\text{Al}_2\text{O}_3\text{--CeO}_2$ catalysts CO was not detected at all during the activity tests. With $\text{Pd}/\text{Al}_2\text{O}_3$ and $\text{Pd}/\text{Al}_2\text{O}_3\text{--TiO}_2$ catalysts the highest measured CO yields were 10% at 408 °C (Fig. 8b) and 3% at 332 °C, respectively. With Rh catalysts CO formation varied a lot: maximum CO yields detected were 46% over $\text{Rh}/\text{Al}_2\text{O}_3$ (Fig. 8c), 14% over $\text{Rh}/\text{Al}_2\text{O}_3\text{--TiO}_2$ and only 1% over $\text{Rh}/\text{Al}_2\text{O}_3\text{--CeO}_2$. Depending on the catalysts, CO formation started from the temperature above 220 °C, and as expected, decreased later on and the selectivity towards CO_2 improved as the temperature was raised. Over $\text{Pt}/\text{Al}_2\text{O}_3$ (Fig. 8a) and $\text{Pt}/\text{Al}_2\text{O}_3\text{--CeO}_2$ catalysts CO was not detected any more at above temperatures of 440 °C and 460 °C. Over all the supports and all the V_2O_5 catalysts CO formation was still observed when the test was stopped at 700 °C (or at 600 °C for vanadium containing catalysts).

3.6. Stability in DCM oxidation

Based on the activity experiments, the most active and HCl selective catalyst, $\text{Pt}/\text{Al}_2\text{O}_3$ was chosen for a long-term stability test in DCM oxidation in moist conditions at constant temperature of 400 °C. No obvious decrease in the catalyst performance was seen during the 40.3 h test (Fig. 9). The DCM conversion stayed stable between 91 and 96% and the HCl yield remained relatively constant fluctuating from 82% to 90%. Moreover, there was no detectable deterioration in the selectivity during the stability test. Also CO formation stayed stable as the measured CO yield was ~2% during the whole test.

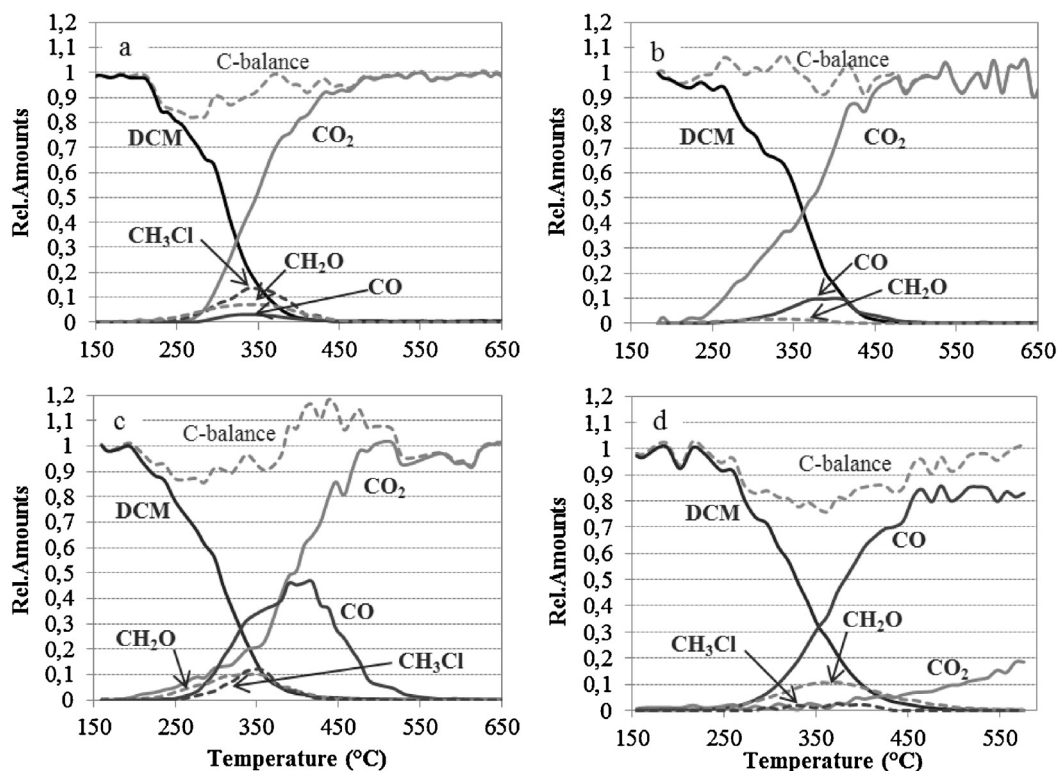


Fig. 8. DCM oxidation over (a) Pt, (b) Pd, (c) Rh and (d) V_2O_5 catalyst supported on Al_2O_3 (the same conditions as in Fig. 5).

FESEM and EDS-mapping images of the fresh and aged Pt/ Al_2O_3 catalysts are shown in Fig. 10a–b. The EDS-mapping indicated that platinum was well dispersed on the catalysts' surface. The measured platinum dispersion for the Pt/ Al_2O_3 catalyst was 49% [3] (see also Fig. 1). Some visible differences were seen between the FESEM images, as after the 40.3 h stability test the catalyst surface looked somewhat smoother than the fresh surface and the smallest particles visible in Fig. 10a were not present in Fig. 10b. This observation was supported by the fact that after 40.3 h in DCM oxidation the specific surface area (S_{BET}) of the catalyst decreased by ~9%, from $183\text{ m}^2\text{ g}^{-1}$ to $167\text{ m}^2\text{ g}^{-1}$ (Table 2). In Ref. [3] it was shown that over the Pt/ Al_2O_3 catalyst the pre-treatment procedure from RTP to 700°C lowered the specific surface area by ~5%. Therefore the loss of surface area during the DCM oxidation can be estimated to originate from both the pre-treatment, which was also done to this specific sample before ageing, and the long-term experiment. The loss of catalytic material and therefore the loss of surface area coming from handling the metallic monolith, e.g. rolling and un-rolling

the sample (see Fig. 1 in Ref. [5]) can be now ruled out since the N_2 physisorption for both sets of catalysts was done with powder samples scraped from the metallic foil. The systematic decrease in all the textural properties (see Table 2) indicates that some sintering occurred during the stability test. However, since the pore-size distributions of fresh and aged samples were practically identical, no significant changes occurred with the size of alumina crystallites. Another difference seen after 40.3 h of testing was that some oxygen was lost or covered and some chlorine was detected on the catalyst surface (Fig. 10b). In elemental analysis with EDS the detected chlorine amounts were always less than 1 wt.%. At this point the observed chlorine on the surface did not affect the catalysts performance since the Pt/ Al_2O_3 catalyst did not lose its activity or selectivity after 40.3 h in the DCM oxidation conditions (Fig. 9). Further, the FESEM–EDS analysis of the samples pre-treated with Pt-sputtering showed no detectable carbon accumulation on the Pt/ Al_2O_3 catalyst's surface after 40.3 h in moist DCM stream.

3.7. DCM decomposition

Under the used reaction conditions the only chlorinated by-product detected during the DCM oxidation was methyl chloride (CH_3Cl) and above 450°C it was not observed anymore. Over Pd/ Al_2O_3 , Pt and Pd supported on Al_2O_3 – TiO_2 and Pt, Pd and Rh supported on Al_2O_3 – CeO_2 catalysts methyl chloride formation was not seen at all. Since Cl_2 was not measured, closing of the chlorine balance was not possible. The other by-product detected with all the catalysts was formaldehyde (CH_2O). As already mentioned, according to van den Brink et al. [13] DCM (CH_2Cl_2) can directly react with hydroxyl groups on alumina leading to formation of adsorbed formaldehyde before its' further disproportionation to methoxy and formate groups. Displaced chlorides can react with surface Al^{3+} or pick up a hydrogen ion to form HCl. The surface formates react further to CO or CO_2 and the surface methoxy species

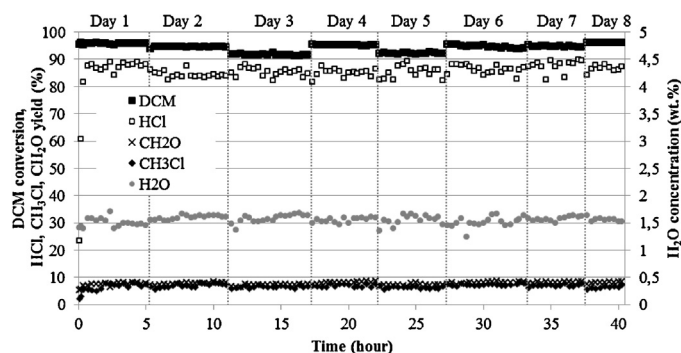


Fig. 9. Stability of Pt/ Al_2O_3 catalyst in the DCM oxidation (400°C , DCM 500 ppm, H_2O 1.5 wt.%, GHSV $32,000\text{ h}^{-1}$).

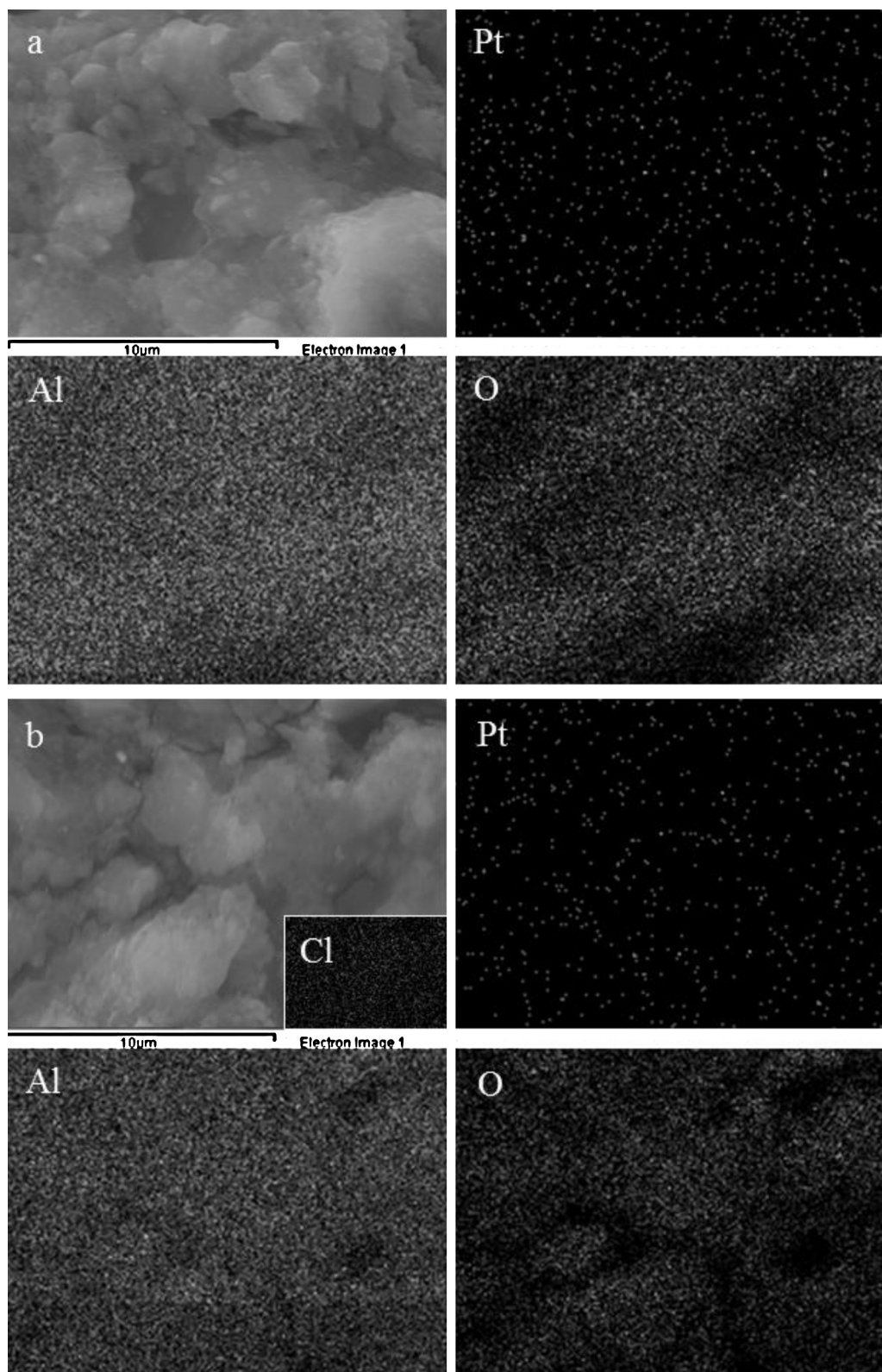


Fig. 10. (a) FESEM image with EDS-mapping of the fresh Pt/Al₂O₃ surface and (b) the same catalyst after 40.3 h stability test at 400 °C.

Table 2
Textural properties of Pt/Al₂O₃ catalysts before and after the 40.3 h stability test.

Sample ^a	<i>S</i> _{BET} (m ² g ^{−1})	<i>V</i> _p (<i>p</i> / <i>p</i> ₀ = 0.990) (mm ³ _{liq} g ^{−1})	PSD type	Mesopore size (nm)	<i>S</i> _(meso) (m ² g ^{−1})	<i>V</i> _(micro) (mm ³ _{liq} g ^{−1})
Fresh	183.1	437	Mono-	7.5	113.3	41.6
Aged 40.3 h (DCM 500 ppm, H ₂ O 1.5 wt.%)	167.0	404	Mono-	7.7	109.3	35.3

^a Parameters were measured for powder catalysts.

can react with HCl to form CH_3Cl . At higher temperatures formaldehyde is rapidly decomposed and more easily desorbed and if methyl chloride is formed, it will be decomposed on $\gamma\text{-Al}_2\text{O}_3$ [13].

Maupin et al. [14] explained the CH_3Cl formation differently: first chlorine from CH_2Cl_2 is substituted by an alumina hydroxyl group (step 1) and then part of the formed chloromethoxy groups are transformed into a hemiacetal species (step 2). After that, hydride is transferred from the hemiacetal species to the chloromethoxy group leading to CH_3Cl formation (step 3) and the formed formate species are decomposed to CO or CO_2 before water is regenerating hydroxyl groups (step 4). In both studies [13,14] it was concluded that water in the feed makes the DCM reaction occurring on the alumina surface as a catalytic reaction by regenerating hydroxyl groups and therefore preventing the deactivation of the catalyst. Water also regenerates some of the aluminium chlorides formed either directly by the reaction of DCM or by reaction of HCl [13].

Based on the detected by-products in this study, the DCM oxidation under the reaction conditions can be assumed to proceed on the catalyst surface via the breakage of the carbon–chlorine bond before the breakage of hydrogen, and hence following the order of the lowest bond energy calculated at room temperature with the HSC Chemistry Software. In our reaction conditions the competition of Lewis acid sites between formaldehyde, DCM and water [12,13] favours DCM and water and formaldehyde is desorbed and detected as a by-product in the gas phase. Also, the reaction between Al and Cl is most likely taking place, since both HCl and CH_3Cl start to appear only after the surface concentration is build up to the saturation point (see Fig. 10) as described by both van den Brink et al. [13] and Maupin et al. [14]. Also the FESEM images of $\text{Pt}/\text{Al}_2\text{O}_3$ after 40.3 h in the DCM oxidation showed evenly distributed chlorine on the catalyst surface (Fig. 10b).

DCM decomposition is a bifunctional reaction and it occurs on the support. During the tests, it was clearly seen that the addition of 26 wt.% titania or 23 wt.% ceria enhanced catalysts' activity in DCM oxidation only slightly (Fig. 5a–c, Table 1), but to the product distribution the effect was major. The detected amounts of intermediates (CH_3Cl , CH_2O and CO) were lowered or diminished and their detection temperatures were decreased. This shows that the reducibility, the oxygen storage function and the increased amount of activated oxygen on the catalyst surface [3,4,32–42] together with the strong metal–support interaction [43–47] is beneficial in DCM decomposition. It is known that CeO_2 and noble metals activate oxygen more readily than the alumina [48] and provide oxygen more efficiently to the total oxidation products. This also means, that surface diffusion on the catalyst plays an important role, because the surface intermediates need to move closer to each other to react further. For this reason, increased acidity and good reduction behaviour, enhancement of surface diffusion and oxygen activation of the catalyst should not be forgotten in the development of more active, selective and durable catalysts for DCM oxidation.

4. Conclusions

Totally 15 metallic monoliths containing Pt, Pd, Rh and V_2O_5 supported on Al_2O_3 , $\text{Al}_2\text{O}_3\text{--TiO}_2$ and $\text{Al}_2\text{O}_3\text{--CeO}_2$ were examined in the oxidation of DCM. Following results are highlighted:

- From the different reaction conditions tested the most pronounced effect on the catalyst activity in DCM oxidation and on the selectivity towards desired reaction product HCl was observed with the gas hourly space velocity (GHSV) followed by DCM concentration and then water amount in the feed gas mixture.

- $\text{Pt}/\text{Al}_2\text{O}_3$ was found to be the most active and HCl selective catalyst: 100% conversion was reached at 420°C and the maximum HCl yield detected was 92%. The 40.3 h stability test (500 ppm DCM oxidation in moist conditions) was carried out at 400°C and no obvious change in the $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts performance was seen. No carbonaceous species was observed on the catalyst's surface, but instead, some chlorine was detected that at this point did not affect the catalyst's activity or selectivity.
- A combination of high acidity and increased reducibility leads to a highly active and selective catalyst in DCM oxidation.
- The addition of ceria and/or platinum to the catalyst strongly enhanced the selectivity towards CO_2 and decreased the formation of CH_3Cl , CH_2O and CO.
- The DCM decomposition during the oxidation and in the presence of an additional hydrogen source seems to proceed on the catalysts' support via detaching the chlorine atoms before the breakage of the hydrogen bonds, hence following the order of the lowest bond energy in each step. Pt, Pd or Rh is needed in the oxidation step of the reaction to ensure CO_2 formation.

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